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Demulsification of O/W Emulsion by Weak Electrostatic Field

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弱い静電場による水中油滴エマルションの解乳化：油滴表面に吸着したイオンによって安定化している O/W エマルションは、弱い電場を印加すると速やかに水相と油層に分離することを発見した。また、この現象が、油滴表面の電荷が電場によって移動したことによる、反発的電気2重層力の消滅により生じることを理論的に明らかにした。

1 Introduction

Although emulsion systems have been widely used in many industrial fields, the formation of emulsion is not always desirable in chemical industries. Formation of emulsions in solvent extraction processes is especially undesirable, since the processes are stopped until the emulsions are separated into oil and water. Electrical demulsification is one of the most convenient ways of separating emulsions into oil and water. However, this has been believed to be operative to only water-in-oil (W/O) emulsions under very high electrostatic fields.

We have recently found that oil-in-water (O/W) emulsions stabilized with ionic surfactants are demulsified by low electrostatic fields of less than 10 V/cm [1-5]. We will show here the experimental and theoretical evidences of proving the demulsification of O/W emulsions by a weak electrostatic field.

2 Experimental evidences

Acceleration of the demulsification of O/W emulsion can be observed on any emulsion systems unless emulsions are stabilized with nonionic surfactants. Figure 1 shows the effect of external DC electric fields on the stability of O/W emulsion that is prepared by shaking the 3 : 2 mixture of oil (1 : 1 mixture of benzyl alcohol and tetrahydropyran) and water (containing 2×10^{-4} mol/dm³ of sodium 2-naphthyl sulfonate as an ionic surfactant) in a separatory funnel more than 100 times. The radii and the zeta potential (ζ) of the oil droplets are 25~30 μ m and 60 mV, respectively. The emulsion layer thus prepared has a lifetime of more than 1 h. The application of a DC electric field of $E_0 > 4$ V/cm shortens the life time to less than 20 s. The acceleration of demulsification is induced neither by electrophoresis nor by electrolysis, since the fusion of the droplets takes place not only near the electrodes but everywhere in the emulsion layer. High frequency pulsed square wave fields also accelerate the demulsification, though it does not for high frequency AC fields. These evidences suggest that the demulsification is induced by the migration of surface charges on the oil droplets.

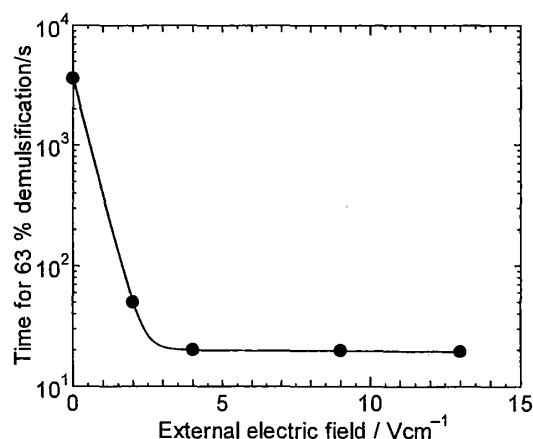


Fig. 1. Effect of external DC electric field on the life time of O/W emulsion.

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3 Theoretical evidence

Fundamental equations for describing the steady-state behavior of ions in O/W emulsions are

$$\nabla \left(\nabla c_{\pm} \pm \frac{ze c_{\pm}}{kT} \nabla \phi \right) = \frac{\partial c_{\pm}}{D_{\pm} \partial t} = 0$$

Smoluchowski diffusion equation for ions in water under electrostatic field ϕ . c_{\pm} and z are the number densities and the valence of the ions, respectively.

$$\nabla^2 \phi = -\frac{\rho}{\varepsilon_l} = -\frac{ez(c_+ - c_-)}{\varepsilon_l}$$

Poisson's equation in water with the dielectric constant ε_l

$$\sigma = \left[z_{s,+} e S_+ \exp \left(-\frac{z_{s,+} e \phi}{kT} \right) - z_{s,-} e S_- \exp \left(\frac{z_{s,-} e \phi}{kT} \right) \right]_{\text{surface}}$$

Surface charge density σ given by the Boltzmann distribution of surface ions with the valences $z_{s,\pm}$.

$$\sigma \equiv e(z_{s,+} s_+ - z_{s,-} s_-) = \left[\varepsilon_l \frac{\partial \phi_i}{\partial n} - \varepsilon_o \frac{\partial \phi}{\partial n} \right]_{\text{surface}}$$

Boundary condition on the surface. s_{\pm} , ε_i and ϕ_i are the surface ion densities, the dielectric constant and the electrostatic potential for oil, respectively

According to the DLVO theory, the electrostatic force acting between the surfaces of approaching oil droplets (the electrical diffuse double layer force) separated by x is given as a sum of the Maxwell's electric field stress and the osmotic pressure as

$$P = -\frac{\varepsilon_l}{2} \left(\frac{d\phi}{dx} \right)^2 + kT c_0 \left[\exp \left(-\frac{ze\phi}{kT} \right) + \exp \left(\frac{ze\phi}{kT} \right) - 2 \right]$$

Using several plausible approximations, the potential energy for the approach of two oil droplets is given by

$$U = \frac{\varepsilon_l \kappa \zeta^2 e^{-\kappa w}}{8(h+1)} \left[\frac{[4(h+1) + 3h(a_1 - a_2)E_0 \cos \eta / \zeta]^2}{h+1 + (h-1)e^{-\kappa w}} - \frac{[3h(a_1 + a_2)E_0 \cos \eta / \zeta]^2}{h+1 - (h-1)e^{-\kappa w}} \right] - \frac{A_H}{12\pi w^2}$$

where $h = z_s e \zeta (s_{+,0} + s_{-,0}) / [kT (s_{+,0} - s_{-,0})]$; κ , the Debye reciprocal length; w , the separation distance between the front surfaces of approaching two droplets with radii a_1 and a_2 ; E_0 , the intensity of the external electric field; η , the angle between the axis of approach and the external field; and A_H , the Hamaker constant of the droplets, respectively. The above equation indicates that the repulsive double layer force, the origin of stabilizing charged emulsion particles, changes to be attractive by applying the external electric field of

$$|E_0| \geq \left| \frac{2[z_s e \zeta (s_{+,0} + s_{-,0}) + kT (s_{+,0} - s_{-,0})]}{3z_s e (s_{+,0} + s_{-,0}) a} \right|$$

where a is the radius of the larger droplet. A weak external electric field thus demulsifies charged O/W emulsions.

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